

# FLUORESCENT PROBES FOR MONITORING MICROSTRUCTURE OF POLYMER/CLAY NANOCOMPOSITES\*

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## Abstract

A fluorescent dye, Nile Blue (NB), was used as molecular probe to monitor the microstructure of organo modified montmorillonite clays as they were compounded with nylon 11. Prior to compounding, the dye was incorporated into the gallery between silicate layers of the clay by an ion exchange process. The NB doped clays had no fluorescence due to concentration quenching. But, upon compounding the clay with nylon 11, the dye was released from the clay galleries during intercalation of the polymer and exfoliation of clay platelets. The process of exfoliation was monitored during compounding by measuring the fluorescence spectrum as a function of time. Experiments were carried out using a batch mixer that was instrumented with an optical fiber sensor.

## Introduction

The principle objective when compounding polymer/clay nanocomposites is to produce a composite with exfoliated or intercalated clay microstructure that yields enhanced properties of the product.(1) Determining microstructure involves off-line X-ray and transmission electron microscope (TEM) measurements. One can minimize off-line characterization by using on-line, real-time measurements from which microstructure can be deduced. Fluorescent probe molecules that are sensitive to their micro and nanostructure environment are candidates for reporting on the state of microstructure through their fluorescence spectra.

Organo modified montmorillonite clays possess silicate layers that are separated in accordance with the size of the organic surfactant modifier that is placed in the gallery region between them. In naturally occurring clays the negatively charged silicate surfaces are neutralized with Na<sup>+</sup> and K<sup>+</sup> and Mg<sup>++</sup> ions. The highly polar natural clays do not exfoliate when mixed with organic polymers because the enthalpy/entropy thermodynamic conditions are not satisfied. However, by ion exchange process, quaternary organic ammonium ions can replace the natural ions yielding galleries of larger dimensions and compatibility with organic resins. The ion exchange process is also the mechanism by which we have incorporated Nile Blue perchlorate into the clay galleries. Our objective is to obtain fluorescence spectra as a function of processing

parameters and as a function of the resultant clay nano and microstructures.

The properties of photosensitive dyes in intercalation have been the subject of many studies that provide a background for the approach that we take here using Nile Blue A (NB), a perchlorate fluorescent dye. It is known that NB will experience significant blue shift in its spectrum when placed in nanoconfined regions of less than 7.5 nm.(2) At elevated concentrations NB can form a dimer or H-structure that is non-fluorescent, and concentration quenching can also occur.(3) The demonstrated sensitivity of NB to its micro-environment makes it a likely candidate for a microstructure probe of polymer clay nanocomposites. Preliminary results using NB as a structure probe were reported in a previous publication.(4)

## Experimental Procedure<sup>a</sup>

Closite 15A and 30B clays, which were obtained from Southern Clay Products, are montmorillonite clays modified by a ion exchange process that incorporates a quaternary ammonium ion, (dimethyl, dihydrogenatedtallow), into the gallery region. Standard ion exchange procedures using aqueous ethanol were modified for the preparation of the 15A clay with NB.(5) Nile Blue A perchlorate was obtained from Aldrich, and incorporated in the clay gallery by a second ion exchange that was designed to replace 1 % of the 15A or 30B surfactant with NB dye.

Nylon 11, Rilsan BESNO, was obtained from Atofina. The powdered clay was compounded with the polymer at 4 % mass fraction of clay in the polymer. Compounding was carried out using a Haake Reocord model 9000 batch mixer. The Haake batch mixer was instrumented with an optical fiber sensor for retrieving fluorescence spectra in real time.(6) The spectra were obtained using the Ocean Optics model 2000USB spectrometer. The fluorescence excitation light was generated at 407 nm by a 30 mw diode laser from Power Technologies. The relative uncertainty of the fluorescence intensity

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<sup>a</sup> Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

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measurements after subtraction of the background is 2 %. Microstructure of the compounded nylon 11/15A nanocomposite was examined using a transmission electron microscope (TEM).

## Results

Figure 1 is a TEM of a nanocomposite that was compounded for 5 min at 195 °C. Extensive exfoliation of the clay is visible, but there are also particles consisting of several silicate layers and larger aggregates. In addition, the compounded product contained clay particles that were visible to the naked eye. The microstructure, while containing a substantial amount of exfoliation, is not fully exfoliated and consists of a combination of exfoliated, intercalated and aggregate particles.

Figure 2 is a fluorescence spectrum of the 15A/NB clay taken at room temperature after ion exchange incorporated the dye in the clay. The absence of significant fluorescence is attributed to high concentration of dye clusters in the gallery that resulted in concentration quenching. A spectrum, taken at room temperature after mixing the clay with nylon 11 for 10 min at 195 °C, is shown in Figure 3. By comparison with Figure 2, it is clear that the NB dye molecule in the compounded material is not quenched and displays significant fluorescence. Our interpretation of this result is that, during compounding, the dye molecules are released from the gallery regions if exfoliation occurs. This result, in conjunction with the TEM observation, supports our hypothesis that exfoliation is necessary for the expression of fluorescence. Similar observations were obtained previously using nylon 6 as the matrix.

The results of real-time monitoring of mixing in the Haake batch mixer at 195 °C are shown in Figure 4. Here, the change in the spectra over a period of 10 min of compounding shows the development of the fluorescence. In particular, two peaks in the spectra at 509 nm and 605 nm change in intensity in opposite directions as a function of compounding time. These changes follow the release of dye from the gallery in concentrated clusters that are subsequently dispersed as mixing proceeds. The peak at 605 nm is suppressed by concentration quenching, i.e. by intermolecular dye-dye contact, but became more intense as dispersion of the dye through the matrix proceeded yielding fewer dye-dye interactions.(4) (The differences between the spectra at 195 °C and that at room temperature (Figure 3) are attributed to the temperature difference.(7)) If we plot the ratio of the intensities at 605 nm and 509 nm,  $I_{605}/I_{509}$ , versus time, we obtain the plot shown in Figure 5. The data show that, after 10 min, the exfoliation/mixing process has not reached completion. At long times, it is possible that two phenomena contributed to the positive slope of the curve: one, the dye molecules became more disperse minimizing dye interactions, and two, exfoliation continued to occur.

The results from compounding 30B/NB clay with nylon 11 are shown in Figure 6. In contrast to the data seen in Figure 4 for 15A/NB clay, the fluorescence intensity at 605 nm remained relatively small compared to that at 509 nm, although a shoulder in the curve was observed in the vicinity of 605 nm. Plotting the ratio,  $I_{605}/I_{509}$ , versus time for 30B/NB clay mixed with nylon 11 gives Figure 7. We see that, while there is some change in the ratio over the time, it is small compared to the change seen in Figure 5. We conclude that the 30B/nylon 11 composite had substantial aggregate and intercalated microstructure that did not allow the NB dye to migrate from the gallery. The limited extent of exfoliation in this composite is confirmed by dielectric and light transmission observations that we obtained during real-time process monitoring, work that is the subject of another presentation at this meeting.(8)

## References

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Keywords: nylon 11, clay nanocomposites, fluorescence, process monitoring

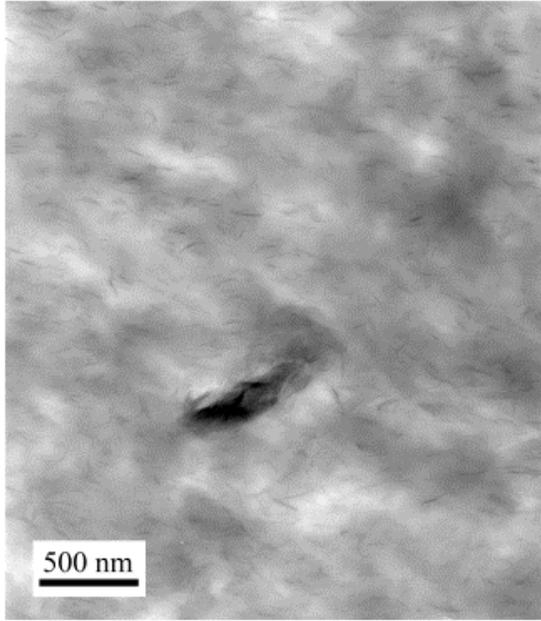


Figure 1. TEM of nylon 11 compounded for 5 min with 15A clay.

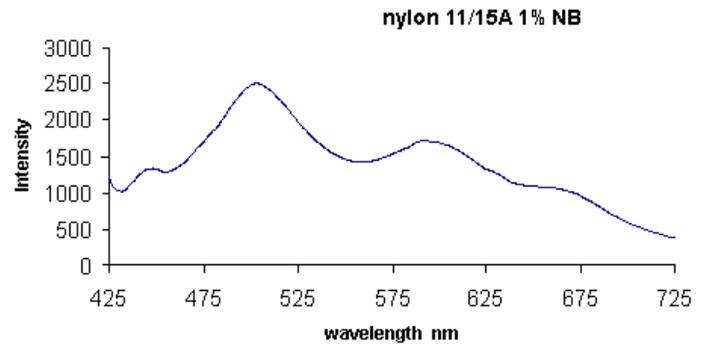


Figure 3. Fluorescence spectrum of nylon 11 compounded with 15A containing NB dye. Spectrum was obtained at room temperature.

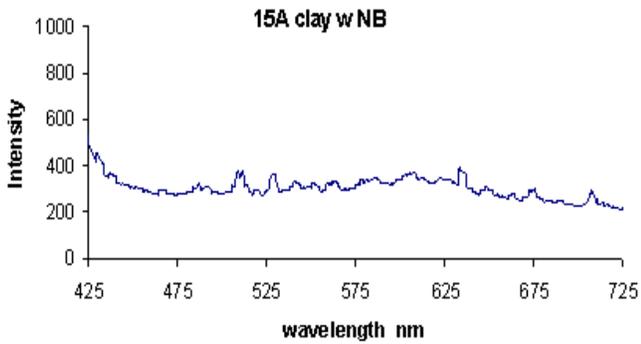


Figure 2. Fluorescence spectrum of 15A clay containing 1 % NB dye. Spectrum was obtained at room temperature

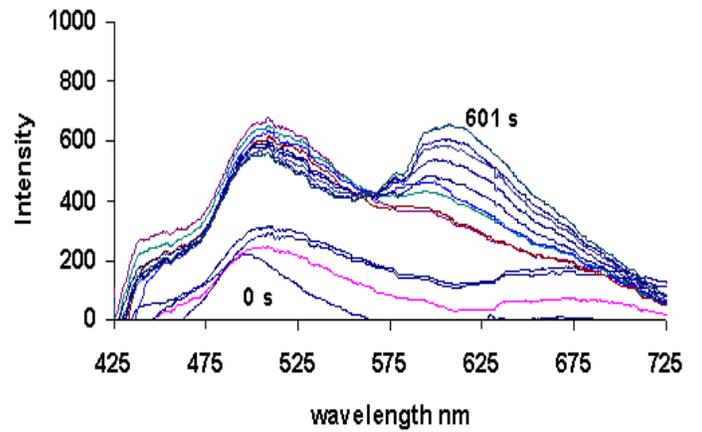


Figure 4. Fluorescence spectra obtained during mixing of nylon 11 with NB doped 15A clay at 195 °C. Thirteen spectra were obtained over a ten minute period.

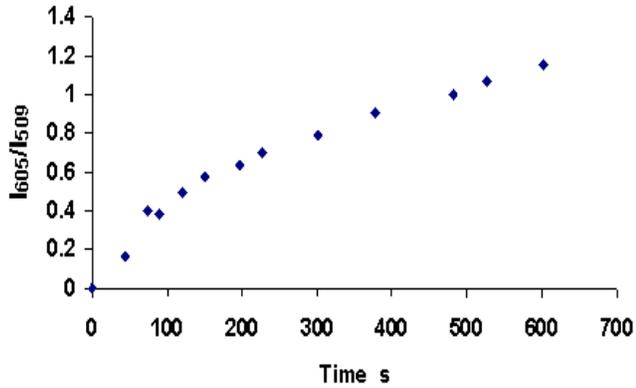


Figure 5. The ratio of fluorescence intensities at 605 nm and 509 nm are plotted versus mixing time for NB 15A clay mixed with nylon 11.

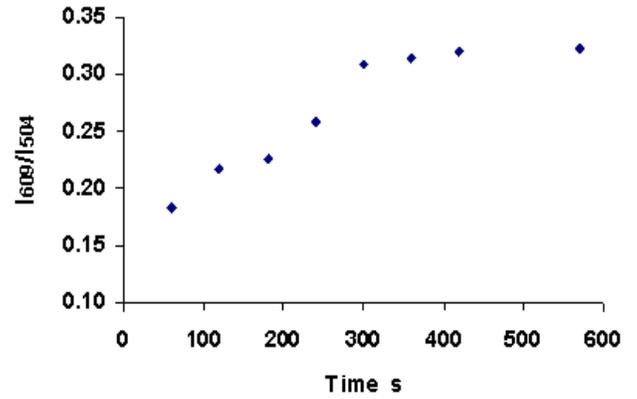


Figure 7. The ratio of fluorescence intensities at 605 nm and 509 nm are plotted versus mixing time for NB 30B clay mixed with nylon 11.

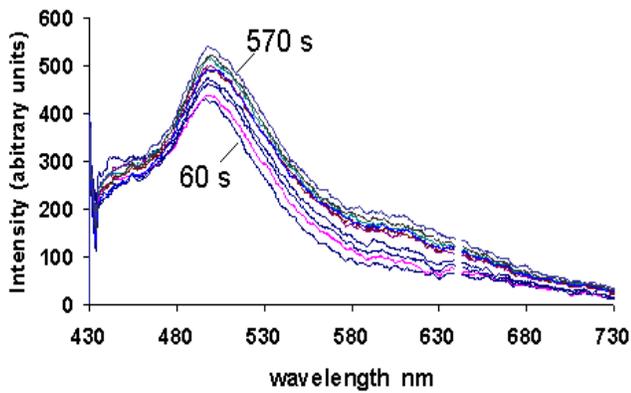


Figure 6. Fluorescence spectra obtained during mixing of nylon 11 with NB doped 30B clay at 195 °C. Eight spectra were obtained over a nine minute period.